UTILIZATION OF WASTE

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CERAMIC MIXTURES CONTAINING CULLET FOR DECORATIVE MAJOLICA

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The author considers the possibility of decreasing the porosity and increasing the mechanical strength of majolica mixtures based on Gzhel'skii deposit clays with 3 – 10% cullet additive. The ceramic properties of the obtained articles meet all technical requirements imposed on majolica products.

Some previously developed majolica mixtures contained 10 – 40% cullet and had decreased porosity [1]. The minimum water absorption value (less than 6%) in these mixtures was observed within the temperature range of 950 – 1000°C.

The purpose of the present study was to obtain majolica with lower porosity and increased strength.

For this purpose, the variations in the physicomechanical properties (porosity, mechanical strength, shrinkage, etc.) of majolica mixtures were studied in decreasing the content of the introduced additive (cullet) from 10 to 3%. The batch compositions of the mixtures (Table 1) are represented by the polymineral low-melting Gzhel'skoe clay and cullet, which is glass waste from an electric bulb factory.

The experimental mixtures were milled in two stages in a ball mill: first, cullet with 5% clay was subjected to milling to 2 – 3% residue on a sieve No. 0056, after which the rest of the clay was loaded. The experimental majolica mixtures by their granulometric compositions can be classified as low-dispersion mixtures (Table 2).

In firing at temperatures ranging from 800 to 1020°C, it was found that the fire shrinkage of the experimental mixtures depends directly on the temperature and the additive content, i.e., as the temperature and the cullet content grow, the fire shrinkage increases. At the same time, with an increasing cullet content, the air shrinkage decreases from 10.5 to 9.0 %.

The maximum strength (62.8 MPa) was seen in mixture samples containing 10% cullet fired at temperature 1020°C, and the minimum strength (32 MPa) was observed in mixture samples containing the lowest amount of the additive (3%), since the strength of the mixture decreases with the decreasing content of the additive, although the maximum strength of this mixtures in the air-dry state is 7.6 MPa (as distinct from the other mixtures). This can be accounted for by the different behavior of the additive before and during firing, i.e., the cullet before firing acts as a grog component: the greater the amount of the additive in the mixture, the lower its mechanical strength in the air-dry state. The additive in firing contributes to the formation of the vitreous phase in the ceramic structure, thus behaving as a flux, and consequently, with increasing cullet content, the mechanical strength becomes higher.

The microscopic study of mixture 2 shows that its structure (Fig. 1) is rather homogeneous, the quartz grains reach a

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TABLE 1

Mixture	Variegated clay : cullet	Milling fineness, %	Mechanical strength, MPa		Shrinkage in air-dry state, %	Shrinkage, %, at temperature,°C				
			in air-dry state	at 1020°C		850	900	950	980	1020
1	90 : 10	1.1	4.7	62.8	9.0	1.3	2.3	3.5	3.8	4.3
2	93 : 7	1.0	5.2	39.0	9.6	1.2	2.0	3.1	4.0	4.2
3	95 : 5	1.2	5.7	35.9	10.0	1.1	1.8	2.6	3.3	4.4
4	97 : 3	1.0	7.6	32.0	10.5	0.8	1.6	2.4	2.7	3.0

TABLE 2

Mixture	Particle content, %, of size, μm				
	< 1	1 – 5	5 – 10	10 – 20	20 – 40
1	36	30	18	12	4
2	32	30	21	13	4
3	38	29	17	11	5
4	32	30	20	13	5

size ranging from 5 – 10 to 50 – 150 μm, and the carbonate grains from 10 – 20 to 10 μm; firthermore, aggregates of hydromica and chlorite are encountered. The pores are uniformly distributed, the size of isometrically shaped open pores ranges from 30 – 45 to 50 – 100 μm.

The porosity of the fired samples was measured through water absorption.

The experimental mixture samples were fired at temperatures 800, 850, 900, 950, 980, and 1020°C. As a consequence of firing, a direct dependence, i.e., a decrease in water absorption, as the firing temperature and the cullet content increased, was observed in all samples. It can be seen in Fig. 2 that the sintering of experimental mixtures starts in the temperature interval 980 – 1020°C, and mixture 1, unlike other mixtures, has the minimum water absorption (4 – 5%). It should be noted as well that whereas at 1020°C the water absorption in all mixtures is approximately equal and constitutes 4 – 7%, at 980°C a spread in values from 5 to 11% is registered.

Thus, a necessary condition for decreasing the porosity in mixtures containing up to 10% cullet consists in firing the mixtures at a temperature not less than 1000°C.

Dilatometric studies demonstrated that the TCLE of the experimental mixtures with different cullet content is virtually equal: $(7.00 – 7.24) \times 10^{-6}\ K^{-1}$ in the temperature range of 20 – 400°C. The TCLE of these mixtures agrees well with the TCLE of the glaze used at the Gzhel' Company to coat pottery and majolica products. Furthermore, the glazed majolica products made of the experimental mixtures with cullet additive after a second firing have a high thermal resistance.

As a result of industrial testing of majolica mixture 2 containing 7% cullet at the Ghzel' Company, molding moisture was determined for various molding methods. Thus, in molding large-sized articles on the mechanized line, the mixture moisture should be 25.0 – 26.5%, and in manual molding the moisture should be 26 – 28%, depending on the complexity of the article shape. The resulting articles satisfied all requirements imposed on majolica products.

Thus, ceramic mixtures based on clay from the Gzhel'skoe deposit with a cullet additive are suitable for ornamental ceramics at a firing temperature of 980 – 1020°C.

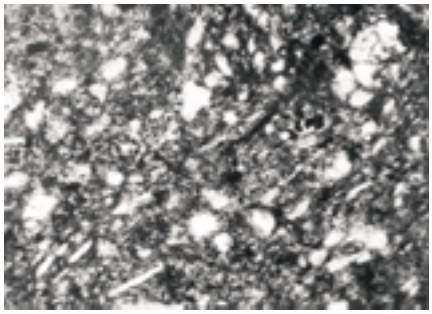

Fig. 1. Structure of mixture with glass cullet.

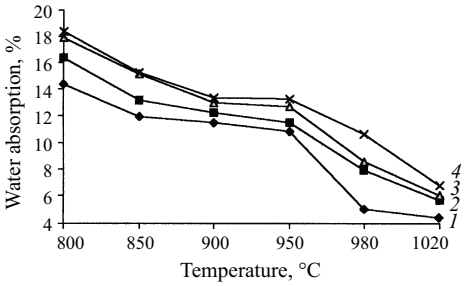

Fig. 2. Dependence of water absorption of mixtures on temperature. Curve numbers corresponds to mixture compositions.

REFERENCES

1. N. S. Yugai and V. M. Loginov, "Ceramic mixtures with decreased porosity for decorative majolica," *Steklo Keram.*, No. 2, 15 – 17 (2001).